

NO-1194 318

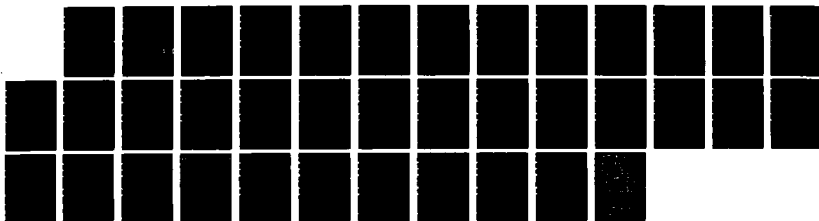
THE ELECTROCHEMICAL BEHAVIOR IN AQUEOUS MEDIA OF
CONDUCTING POLYMERS 2 TH (U) UTAH UNIV SALT LAKE CITY
DEPT OF CHEMISTRY S PONS ET AL 30 JUL 86 TR-80

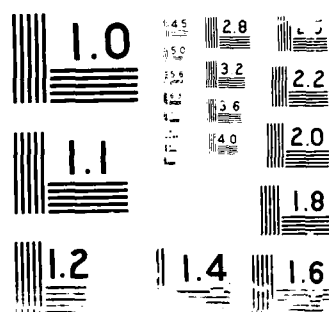
UNCLASSIFIED

N00014-83-K-0470

F/G 7/6

NL





ONE FILE COPY

AD-A194 318

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470-P00003

Task No. NR 359-718

TECHNICAL REPORT # 80

The Electrochemical Behavior in Aqueous Media of Conducting Polymers:
II: The Insoluble Fractions Obtained on the Cu(II) Catalyzed
Polymerization of (2,5-Dibromo-3-Group IV Substituted) Thiophenes

By

Stanley Pons, A Czerwinski, D. Cunningham, A. Amer, J. Schrader
C. Pham, H. Zimmer, H. Mark, Jr.

Prepared for Publication in
Journal of the Electrochemical Society

University of Utah
Department of Chemistry
Salt Lake City, Utah 84112

July 30, 1986

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

DTIC
ELECTE
S APR 14 1988
H

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 80	2. GOVT ACCESSION NO. ADA194318	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Electrochemical Behavior in Aqueous media of Conducting Polymers: II: The Insoluble Fractions Obtained on the Cu(II) Catalyzed Polymerization of (2,5-Dibromo-3-Group IV Substituted) Thiophenes		5. TYPE OF REPORT & PERIOD COVERED Technical Report # 80
7. AUTHOR(s) Stanley Pons, A Czerwinski, D. Cunningham, A. Amer.		6. PERFORMING ORG. REPORT NUMBER
9. 1. DEPENDENT ORGANIZATION NAME AND ADDRESS University of Utah Department of Chemistry Salt Lake City, UT 84112		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0470-P0003
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 359-718
12. REPORT DATE July 30, 1986		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Conducting Polymers, Polythienylenes, Polymer Electrodes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Substituted thiophenes are used as electrode material: the redox chemistry of copper containing polymer in contact with the electrolyte shows only internal copper chemistry.		

THE ELECTROCHEMICAL BEHAVIOR IN AQUEOUS MEDIA OF CONDUCTING
POLYMERS: II; The Insoluble Fractions Obtained on
the Cu(II) Catalyzed Polymerization of
(2,5-Dibromo-3-Group IV Substituted) Thiophenes

Andrzej Czerwinski⁺, David D. Cunningham*, Adel Amer[‡],
John R. Schrader, Chiem Van Pham, Hans Zimmer
and Harry B. Mark, Jr.*

Department of Chemistry
University of Cincinnati
Cincinnati, Ohio 45221

Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Abstract

The chemical polymerization of (2,5-dibromo-3-substituted) thiophenes utilizing Cu(II)Cl₂ as a copromoter yields an amorphous insoluble polymer fraction which exhibits a very high electronic conductivity varying between 10⁻¹ to 10² S-cm. These materials have been used as electrode materials. The redox chemistry of the Cu(II) containing polymer in contact with supporting electrolyte only shows a distinct internal (Cu(II)/Cu(I) cyclic voltammetric wave. No redox behavior for the thiophene ring system is observed. This material is very stable in aqueous media and appears to be conducting at positive and negative electrode potentials (contrary to the redox response of electrodeposited polythienylene films). The lack of 3-substituent steric effects is discussed. The similarities and, more important, the dissimilarities of the properties of these polymers and Cu(II)-dithiolate complexes are also discussed. ←

⁺ On leave of absence from the University of Warsaw, Warsaw Poland

[‡] On leave of absence from the Alexandria University, Alexandria, Egypt

* Electrochemical Society Active Member

Key Words: Conducting polymers, polythiénylenes, polymer electrodes, aqueous media, 3-substituted 2,5-dibromothiophenes, Cu(II)/Cu(I), redox couple, substituent effects, and Cu(II)-dithiolate complexes.

In recent years an extensive interest and research on the synthesis and electrochemical properties of macromolecules with extended π -electron systems has been reported (1). In particular, the majority of the research involved polymers with systems of conjugated π -electrons which, upon doping, form charge transfer complexes (2,3). These can exhibit semiconducting or metallic conducting properties (3-5).

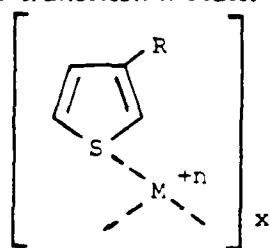
The first well characterized conducting polymer system was poly(sulfur nitride), $(\text{SN})_x$, (6-8) which was reported in the 1970's. The first conducting organic polymer system synthesized was poly(acetylene), -(CH=CH)_x which can undergo both n- and p-type doping. The conductivity of the poly(acetylenes) depends on the concentration and chemical nature of the dopant (9,10). Other conjugated π -electron systems with similar properties are poly(p-phenylene), $\text{-(C}_6\text{H}_4\text{)}_x\text{-}$ (11), and poly(p-phenylene vinylene), $\text{-(C}_6\text{H}_4\text{CH=CH)}_x$ (12). These doped materials have limited stability (12). A very stable polymer film of poly(pyrrole), formed on electrooxidation of pyrrole on a platinum electrode, has been reported by Diaz et.al. (13). The neutral form of the polymer is an insulator, but on electrooxidation in nonaqueous media the film incorporates anions and exhibits high conductivity (14). Electrodeposited films of poly(thiophene) have electrical conductivity properties comparable to the poly(pyrrole) film. For polymerization and also for anion incorporation more positive potentials are required (15-17). However, when exposed to ambient conditions for a few weeks, these films lose their conductivity and electrode activity.

In connection of one of the results in this communication it is of interest to note that some reports indicate the inclusion of CuCl_2 in the electrolyte improves the electropolymerization of benzene and naphthalene (18,19).

Recently polymeric materials obtained by transition metal induced polymerization of the bis-Grignard compounds derived from 2,5-dibromothiophene and 2,5-dibromo-3-methyl thiophene have been reported by Yamamoto et al. (20,21). After iodine doping these poly(2,5-thienylenes), have been shown to exhibit significant conductivity. Interestingly, the polymers were very stable, and the authors commented that some of the

transition metal catalyst incorporated in the polymer could not be removed or exchanged by chemical treatment. Zimmer et al. (22,23) devised a modification of the synthetic route by employing the 2,5-dilithiothiophenes in place of the bis-Grignard compounds. Subsequent anhydrous metal salts promoted polymerization producing materials which on iodine doping showed improved conductivity as compared to the materials prepared according to Yamamoto et al. In addition, these materials exhibited an extraordinary degree of stability.

In continuation of our interests in investigating conducting polymeric materials containing bonded redox centers for theoretical studies as well as potential electrocatalytic surfaces, we have synthesized a series of poly(3-substituted-2,5-thienylenes) containing various incorporated transition metals. The general unit monomer structure is:



Where R = -H, -CH₃, -Si(CH₃)₃, -Ge(CH₃)₃ and -Sn(CH₃)₃ for the Cu(II) containing polymers, and M = Cu(I), Cu(II), Mo(VI), Ru(III), Fe(III), Co(II), Ni(II), and Pt(IV) for 3-methyl-polymers. This paper, for reasons discussed below, deals principally with the Cu(II)-polymer series because of their unique electrochemical properties (24). Furthermore, this paper will deal only with the insoluble amorphous polymer fraction obtained from the synthesis. The electrochemical behavior of the methanol soluble Cu(II)-poly(3-methyl-2,5-thienylene) is different and is reported elsewhere (25). This paper will examine the redox behavior of incorporated Cu(II) upon electrochemical polarization in aqueous media; it also will demonstrate the electrical conductivity of this material by the cyclic voltammetry of the ferro/ferricyanide couple in the electrolyte phase. The effects of pH, potential sweep rate, prolonged electrolysis and storage conditions on stability, valence state of the incorporated copper, the nature of the 3-substituent, and the lability of the incorporated Cu(II) will be presented.

Experimental

The synthesis of the various 3-substituted-2,5-dibromothiophene monomers followed published procedures (26). The polymerization of the monomeric dibromo analogs utilizing n-butyllithium and transition metal catalysts and the isolation of the insoluble polymer fractions has also been previously reported (22,23).

The dried amorphous insoluble polymer fraction was pressed into pellets using a standard IR pellet dye under 5000 psi pressure. The polymer pellets were mounted in an electrode assembly system that has previously been described (27). All solutions were deaerated with argon unless otherwise specified. Potentials were measured at $20 \pm 1^\circ\text{C}$ vs the saturated calomel electrode, SCE. For the i-E studies, a BAS model CV-1B-120 voltammetry controller and Hewlett-Packard model 136A x-y recorder were used.

Results and Discussion

In Figure 1 cyclic voltammograms for the insoluble polymer fraction of poly(2,5-thienylene) are shown. The material was obtained by using anhydrous CuCl_2 as the promoter in the polymerization of 2,5-dilithiothiophene (23). We shall demonstrate that the broad peaks are due to the redox reaction of the copper cations incorporated in the polymer matrix. The shape of the peaks also indicates a broad potential range of electrical conductivity in contrast to the polymer films produced on electrooxidation of thiophene (15-17). These curves were generated at two different sweep rates (10 mV/s and 100 mV/s). It is evident that at the lower sweep rate much higher amounts of charge are passed in the electrochemical reactions (Table 1). In Table 1 the amount of charge is listed also for various sweep rates. The supporting electrolyte in these experiments was 0.1 M NaClO_4 . In addition this table contains the formal potentials, E^0 , calculated from cathodic and anodic peak potentials ($E^0 = (E_{pa} + E_{pc})/2$). This data shows that the amount of charge involved in the redox reactions is very strongly dependent on the rate of potential polarization, whereas the E^0 is relatively independent. The amount of charge and the dependence on sweep rate reveal that the copper, not only near the surface of the

polymer, but some in the bulk of the polymer takes part in the redox reaction. It is interesting to note that the X-ray analysis (EDAX) of the surface of cycled electrodes actually showed a slightly increased copper concentration. The bulk copper concentration is about 30% by weight as measured by atomic absorption analysis.

It can be seen in Figure 1 that at the lower sweep rate more peaks or waves appear. These additional small peaks are generally at more negative potentials suggesting that they may be due to the reduction of Cu(I) to Cu(O). These peaks may represent a reduction of Cu(I), but it is not complete, meaning that only a small fraction of the Cu(I) is reduced to Cu(O) on the time scale of this experiment. It is important to note that the main current peaks represent a Cu(II)-Cu(I) redox reaction, and not the main oxidation of an extended π -electron system, such as occurs in electropolymerized poly(thienylenes) (13-17).

Other investigators have reported an increased stability of Cu(I) ions in an electropolymerized poly(thienylene) matrix (28). In Table 2, the formal potential values for several copper catalyzed 3-substituted poly(thienylenes) are presented. Both, Cu(I) and Cu(II) were used to make poly(3-methyl-2,5-thienylene) and voltammograms of the former are shown in Figure 2. After extended cycling the redox couple of the more poorly conducting Cu(I) containing polymer gains definition and shifts to more negative potentials. This indicates a change in chemical environment or structure of the copper coordination geometry is taking place. From these data and the ones from Table 2 it becomes evident that the electrochemical behavior of polymers obtained with Cu(II) significantly differs from polymers obtained in the presence of Cu(I). The good mechanical and chemical stability of the electrodes during long cycling times suggests that Cu(II) as well as Cu(I) is strongly complexed by the polymer.

The polymers listed in Table 2 were designed so that the substituents had a systematic and large variation in size but, as small as possible differences in inductive properties. The only significant difference in inductive effects would occur in going from the 3-H to the 3-CH₃ group. Surprisingly, even the most bulky groups did not hinder the

chemical polymerization or significantly affect the properties of the polymers. The lack of steric effects here is very surprising as bulky 3-substituents, $-\text{C}(\text{CH}_3)_3$ for example, prevent polymer film formation on electrooxidation (29), presumably because of steric hindrance of the 2-position. Also, substituents which varied in their ability to donate to or to withdraw electrons from the aromatic moiety of the polymer had strong effects on the redox potentials of electrooxidized poly(thienylenes) (2). With both steric and electronic effects of the chemically produced matrix being absent the evidence is that the thiophene ring system of chemically polymerized monomeric 3-substituted thiophenes does not undergo a redox reaction.

Figure 3 shows the voltammograms for Cu(II) -poly[3-(trimethylstannyl)-2,5-thienylene] when successively more negative switching potentials are employed. It appears that the oxidation peak cannot be observed without a prior negative scan first. This required first reduction once again supports the opinion that Cu(II) cations are initially incorporated in the polymer and are responsible for the main redox couple.

In Figure 4 data are representative of experiments in which some environmental conditions are varied. It appears that oxygen lowers the redox currents. The redox currents in deaerated solutions are also slightly lower if the electrolyte is stirred. This phenomenon is not understood, however one explanation might be explained by assuming that stirring may stimulate faster diffusion of the Cu(II) cations on or near the surface into the bulk of the solution.

In Figure 5 the concentration of copper leached into the bulk electrolyte is plotted as a function of time. The rate of leaching slows after ca. 30 hr. The total amount of copper leached into solution is only a fraction fraction of the copper incorporated in the polymer, and the polymer can be cycled for several weeks ($\sim 10^5$ cycles) without changing the shape of the voltammogram or the magnitude of the peak currents. This material may be stored in air for several weeks and used again. Also, no observable swelling of the polymer disk was observed on cycling the potential.

It is very characteristic for all of the Cu(II) containing polymers to exhibit increasing redox current peaks during the first few cycles. This phenomena is shown for two polymers in Figure 6. It is thought that this peak growth is due to the time necessary for water to penetrate and saturate the polymer matrix and, perhaps, also to some structural changes. That this is a reversible process becomes evident by the fact that the cyclic voltammograms of a used and dried polymer needs a few cycles before returning to steady state. Thus, emphasizing the fact that water plays a very important role in the conductivity of these polymers. As a matter of fact, water changes the dried polymer from virtually non-conductors to good conductors as was reported by us in a previous paper (24) when it was found that poly(3-substituted-2,5-thieylenes) incorporating Cu(II) exhibit a huge increase in conductivity on "doping" with water going from $10^{-7} \text{ S-cm}^{-1}$ to greater than almost 40 S-cm^{-1} in some cases.

It is well known that some transition metal dithiolate complexes exhibit semi-conducting properties (30,31). The 1,2-dicyanoethylene-1,2-dithiolate complexes are a particularly well studied system and it is interesting to note that the copper complex not only has the highest electrical conductivity but it is also found with solvent molecules of crystallization (30).

In order to further study solvent effects in our polymers the following experiments were carried out. Pressed polymer disks were exposed to different constant humidity environments by suspension above sulfuric acid-water mixtures. The conductivity, as measured by the four point probe method, increased proportionally with relative humidity, and droplets of moisture actually formed on the pellet surfaces at 100% humidity. This unusual water nucleating property is not understood at this time. At present we cannot distinguish whether the water is coordinated, or is in an environment comparable to hydrophilic ionomers, where there is a separate phase containing water molecules and ions within a matrix of nonionic units (32).

Voltammograms were taken in H_2O and D_2O (0.1 M NaClO_4) solutions and are shown in Figure 7. It can be seen that the main redox peaks are separated by an additional

40 mV in the deuterated solvent. Isotope effects considered for other electrochemical systems (33) include: 1) 20% lower diffusion coefficients in the more viscous D_2O , 2) slight differences in the double layer capacity, 3) increased pH (0.41 pH units due to lower auto dissociation) and associated equilibria changes, and 4) large thermodynamic effects due to the stronger deuterium bonds. A 40 mV change is relatively large suggesting a primary isotope effect (34). At present it is not known which of the above effects or, perhaps a combination, predominate.

Voltammograms taken in mixed solvent solutions containing different amounts of water are shown in Figure 8. It can be seen that in the electrolyte which contains smaller amounts of water (75% t-butanol) the redox peaks decrease. In water/acetonitrile solutions (Figure 8) much higher currents and sharper peaks appear which suggests that the internal redox couple is more reversible in water/acetonitrile electrolyte than in water.

In Figure 9 voltammograms in solutions of different pH (0.1 M NaOH and 0.1 M $HClO_4$) are presented. In basic solution (pH=13) the native reduction peak observed in neutral solutions has disappeared. An explanation might be that the $Cu(II)$ cations are coordinated to OH^- anions causing a drastic shift of the redox potential or it could mean that the copper-sulfur bonds have been broken. In pH=1 $HClO_4$ electrolyte it appears that the bulk polymer is irreversibly oxidized.

If the voltammograms are taken in a 0.1 N $NaClO_4$ solution containing 10^{-2} N $K_3Fe(CN)_6$ (Figure 10, curve 1). Two pairs of redox peaks are observed. The more negative pair is typical with respect to peak potentials and shapes of a solution phase ferri/ferrocyanide couple at any solid electrode such as platinum. The more positive couple is at potentials similar to that observed for the internal $Cu(II)/Cu(I)$ couple as would be expected. On removing the same electrode from the 10^{-2} N ferri/ferrocyanide-0.1 N $NaClO_4$ solution, washing it repeatedly with distilled water and immersing it in a 0.1 M $NaClO_4$ electrolyte, the cyclic voltammogram showed only the internal $Cu(II)/Cu(I)$ couple (curve 2). Curve 2 is identical to that of the same electrode initially cycled in

supporting electrolyte only. It is obvious that the current peaks for the internal copper(II/I) couple is reduced when a solution phase redox couple is present. Thermodynamically no such reduction in the peak currents for the Cu(II)/Cu(I) couple should occur. However, if the redox process for the internal Cu(II)/(I) couple is rate limited by anion counterion diffusion and slow compared to electron transfer through the polymer to the solution interface the above results would be expected.

Conclusions

The electronic conducting polymer incorporating Cu(II) produced on the chemical polymerization 3-substituted-2,5-dilithiothiophenes are remarkably good conductors after being "doped" with water (up to 40 S-cm^{-1} for some batches). The same polymers containing other transition metal ions relatively remain, even after "doping" with water poor electronic conductors ($\sim 10^{-7} \text{ S-cm}^{-1}$). Their conductivity however, did not increase by incorporation of water (24), which is a big factor in the increase of conductivity of the Cu(II) promoted poly(3-substituted-2,5-thienylenes).

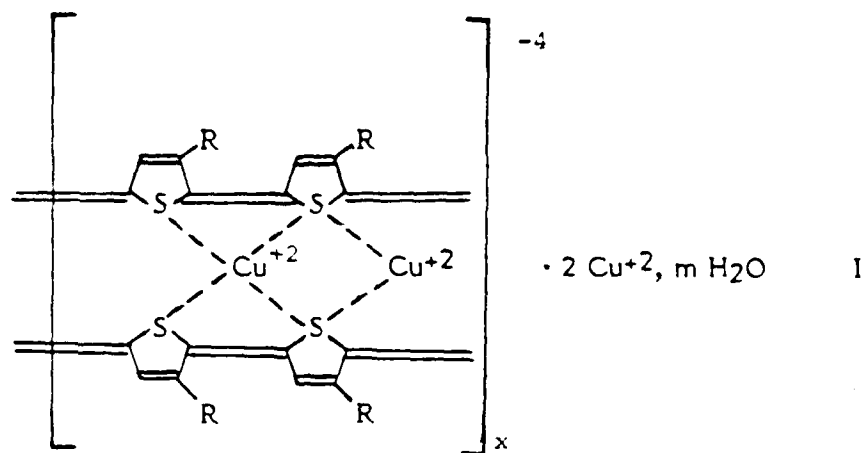
The cyclic voltammograms of the highly conducting polymer exhibit an internal Cu(II)/Cu(I) redox couple and no redox couple for the thiophene ring system. The lack of ring electrochemistry in these polymers may account for the great stability of these materials in aqueous media and even in the presence of oxygen. Presumably the Cu(II) is coordinated to the sulfurs and also acts to crosslink the polymer chains. This probably also contributes to their stability. Surprisingly, there are no significant inductive and steric effects as the 3-substituent on the thiophene moiety is varied. In contrast to electrochemically produced poly(thienylenes), these materials conduct over the entire potential window (about +1.5 to -1.0 V vs SCE).

The microstructure of these polymers and the nature of the copper coordination is not known at this time. The fact that they are extremely stable and not soluble in anything has made it impossible to study them by the usual techniques. However, an interesting comparison of the divalent transition metal dithiolate system and our

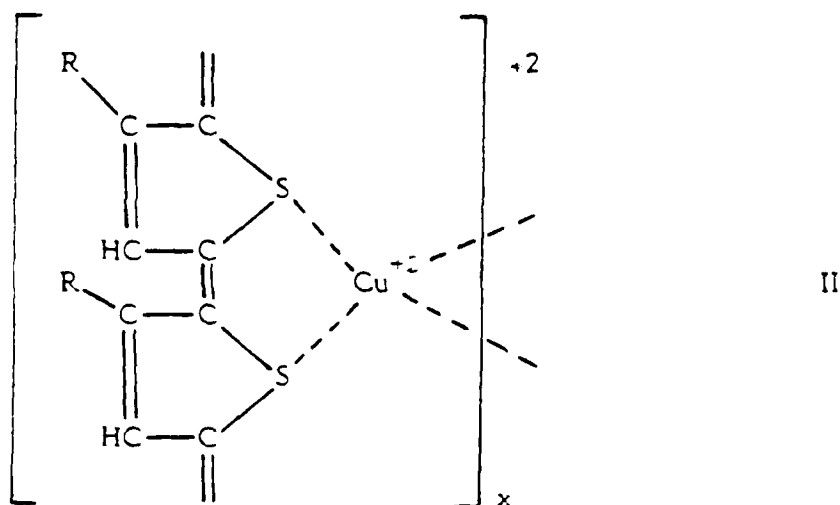
analogous coordinated polymer systems shows structural, electrical, and physical similarities (30). The sulfur-double bond-sulfur structural element common to the best conducting materials (30,31,35), perhaps, is also possible in the poly(thienylene) π -system if the resonance structure with double bonds between the rings would be the predominate one. That this structural element may be important to conductivity of the polymer is corroborated that by the fact that the 1,2-dicyanoethylene-1,2-dithiolates are 10^5 times more conducting than the 2,2-dicyanoethylene-1,1-dithiolate metal salts in which such structure elements cannot occur (30). A frequently observed geometry found for conducting charge transfer salts involves flat complexes stacking one upon another, forming a two dimensional conducting lattice, with the counter ions between parallel planes (36,37,2). All the conducting Cu(II) thiolate complexes are planar, again suggesting the importance an the inter-ring double bonded resonance form of poly(thienylene), which also would be planar.

Our results which show copper superior to other transition metals parallel the findings for the 1,2-dithiolates, where the conductivity for divalent transition metals decreased in the order: $\text{Cu}^{+2} > \text{Co}^{+2} > \text{Ni}^{+2} > \text{Fe}^{+2}$. In similar coordinated polymeric systems the copper complexes exhibited the highest electrical conductivities, up to 40 S-cm^{-1} (31,34). Generally, the dithiolate complexes and coordinated polymers were darkly colored and insoluble in organic solvents and water; thus, their appearance resembles physically the Cu(II)-poly(thienylenes), which even after exhaustive solvent extraction, retain a very high copper content. Two postulated structures are discussed below. One possibility is that copper is both coordinated to the sulfur in an anionic polymer complex and is also ionically situated "outside" the polymer chain, balancing the charge. Water or polar solvent molecules are associated with the cations sited outside the polymer chain facilitating charge-transfer, thereby, increasing the conductivity. This also accounts for the very high Cu(II)-thiophene ring ratio. Also, it is important to note that water content has been shown to have a significance on the electron conductivity for similar $\text{K}_2\text{Pt}(\text{CS})$,

Br_{0.8}·x H₂O systems (38).



However, in spite of this attractive analogy, several experimental facts seem to contradict it. First of all, the model contains chemically bound Cu(II) as shown above. These copper ions would be expected to be readily, if only partially, exchange when the polymer is in contact with electrolyte solutions, such as 0.1 M LiClO₄, etc. No such cation exchange or leaching to any extent is observed. Secondly, on variation of the anion of the solution supporting electrolyte, even with the large Fe(CN)₆⁻³ anion, it was shown that the polymer exchanges the anion (29), which indicates that the Cu(II) polymer matrix is positively charged. Thus, it is more likely that the basic resonance structure in the polymer is:



Although somewhat analogous to the dithiolate salts, there is another distinct difference. This could, therefore, account for the fact that the Cu(II) polymer has at least a 10^5 S-cm⁻¹ better conductivity than the Cu(II) dithiolates. The extended π -system of the amorphous polymer is probably more important with respect to electron conductivity than two dimensional copper-copper interaction. Furthermore, the lack of steric hindrance on chemical polymerization, again in contrast to the electrooxidation polymerization method, indicates that the chemical polymerization proceeds in such a way or rate to yield an organized polymer that does not yield sterically hindered 3,4-substituent units in the polymer (see structure II). This would permit the formation of an extended planar π -system in the polymer itself. It is well known that extended π -system polymers cease to exhibit red shift of optical absorbance beyond about 8 to 9 unit oligomers (39,40). The same is true of the negative shift of oxidation potential for about 5 to 6 unit oligomers(40). The thermal motion of the chain at this point overcomes the stability of the conjugation (39) and larger oligomers exhibit the same optical and electrochemical properties. However, the Cu(II) crosslinking could "freeze" the thermal motion of the polymer and enhance the electron conductivity in the polymer. Separate studies of the electrooxidation of various methyl substituted thiophene oligomers in nonaqueous media have shown that restricted rotation about the 2-5-polymer linkage drastically effect the morphology and electrochemistry of the conducting polymer film (40). Thus, if Cu(II) has a specific orientation effect on the extended π -system, the above results could be expected.

Acknowledgements

We thank the National Science Foundation, Grant No. CHE-8205873 for partial support of this research. We also would like to acknowledge the Lithium Corporation for the donation of n-butyllithium reagent.

References

1. G. Wagner, *Angew. Chem. Int. Ed. Engl.*, 20 361 (1981).
2. R.J. Waltman, J. Bargon, *Can. J. Chem.* 64 76 (1986).
3. J.F. Robinson, H.B. Mark, Jr., A.F. Diaz, *The Electrochemistry of Anisotropic Conductors*, Chapt. on "Extended Linear Chain Compounds", J.S. Miller Ed., Plenum Publishing Co., 198 and references therein.
4. *Proceedings from the International Conference on Low Dimensional Conductors*, *Mol. Cryst. Liq. Cryst.*, vol. 77-79, (1982).
5. Symposium on "Conducting Organic Polymers", Spring Meeting of the Electrochemical Society, Toronto, Canada, May 15-16, 1985, Abstract J. Electrochemical Soc. 132 98C (1985).
6. A.G. MacDiarmid, A.J. Heeger, *Syn. Met.* 1101 (1980).
7. V.V. Walatka, M.M. Labes, J.H. Perlstein, *Phys. Rev. Lett.* 31 1139 (1973).
8. R.J. Nowak, H.B. Mark, Jr., A.G. MacDiarmid, D.J. Weber, *J. Chem. Soc., Chem. Comm.*, 9 (1977).
9. H. Shirakawa, S. Ikeda, M. Aizawa, J. Yoshitake, S. Suzuki, *Syn. Met.* 4 43 (1981).
10. D. MacInnes, M.A. Druy, P.J. Nigrey, D.P. Nairns, A.G. MacDiarmid, A.J. Heeger, *J. Chem. Soc., Chem. Comm.* 317 (1981).
11. D.M. Ivory, G.G. Miller, J.M. Sowa, L.W. Shacklette, R.R. Chance, R.H. Baughman, *J. Chem. Phys.* 71 1506 (1979).
12. O.R. Gagnon, J.D. Capistran, F.E. Karasz, R.W. Lenz, *Polymer Bull.* 12, 293 (1984).
13. A.F. Diaz, J.I. Castillo, *J. Chem. Soc., Chem. Comm.* 397 (1980).
14. A.F. Diaz, J.I. Castillo, A.J. Logan, W.Y. Lee, *J. Electroanal. Chem.* 129 115 (1981).
15. R.J. Waltman, J. Bargon, A.J. Diaz, *J. Phys. Chem.* 87 1459 (1983).
16. A.J. Diaz, *Chemica Scripta*, 17 145 (1981).
17. G. Tourillon, F. Garnier, *J. Electrochem. Soc.*, 130 2042 (1983).

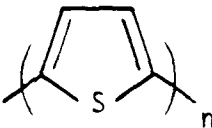
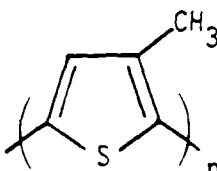
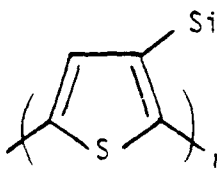
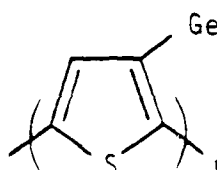
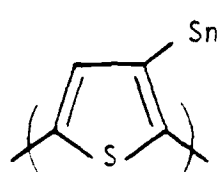
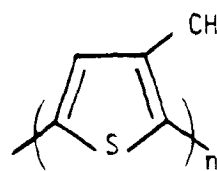
18. M. Satoh, F. Uesugi, M. Tabata, K. Kaneto, K. Yoshino, J. Chem. Soc., Chem. Comm., 550 (1986).
19. M. Satoh, K. Kaneto, K. Yoshino, J. Chem. Soc., Chem. Comm., 1629 (1985).
20. T. Yamamoto, K. Sanechika, A. Yamamoto, J. Polym. Sci., Polym. Lett. Ed., 18 9 (1980).
21. T. Yamamoto Makromol. Chem. Rapid Comm. 6 671 (1985).
22. A. Amer, H. Zimmer, K.J. Mulligan, H.B. Mark, Jr., S. Pons, J.F. McAleer, J. Polym. Sci., Polym. Lett. Ed., 22 77 (1984).
23. C.V. Pham, A. Czerwinski, H. Zimmer, H.B. Mark, Jr., J. Polym. Sci., Polym. Lett. 24 103 (1986).
24. A. Czerwinski, H. Zimmer, A. Amer, C.V. Pham, S. Pons, H.B. Mark, Jr., J. Chem. Soc., Chem. Comm. 1185 (1985).
25. A. Czerwinski, H. Zimmer, C.V. Pham, A. Amer, J.R. Schrader, H.B. Mark, Jr., Anal. Lett. 18 673 (1985).
26. C.V. Pham, R.S. Macomber, H.B. Mark, Jr., H. Zimmer, J. Org. Chem. 49 5250 (1984). The synthesis of 2,5-dibromo-3-trimethylgermylthiophene followed procedures published in this paper; the compound was obtained in 83% yield, b.p. 0.6 Torr 104°C; Anal. Calcd. for: C₇H₁₀Br₂GeS; C, 23.51; H, 2.82; Br, 44.41. Found: C, 23.42; H, 2.93. Br, 44.56.
27. A. Czerwinski, J. Schrader, H.B. Mark, Jr., Anal. Chem. 56 1030 (1984).
28. G. Tourillon, E. Dartyge, H. Dexpert, A. Fontaine, A. Jucha, P. Lagarde, D.E. Sayers, J. Electroanal. Chem. 178 357 (1984).
29. D.D. Cunningham, C.V. Pham, H. Zimmer, H.B. Mark, Jr., in preparation.
30. G. Manecke, D. Wöhrle, Makromol. Chem., 116 36 (1968).
31. G.E. Holdcroft, A.E. Underhill, Syn. Met. 10 427 (1985).
32. E.J. Roche, R.S. Stein, J.W. Macknight, J. Poly. Sci., Polym. Phys., 18 1035 (1980).
33. F.G. Banica, A. Calusaru, J. Electroanal. Chem. 158 47 (1983).

34. T.H. Lowry, K.S. Richardson, Mechanism and Theory in Organic Chemistry 2nd ed., Harper Row, (1981).
35. D. Wohrle, G. Manecke, Makromol. Chem., 140 137 (1970).
36. J.D. Forrester, A. Zalkin, D.H. Templeton, Inorg. Chem. 3 1507 (1964).
37. J.M. Williams, H.H. Wang, M.A. Beno, T.J. Emge, L.M. Sowa, P.T. Copps, F. Behrooz, L.N. Hall, K.D. Carlson, G.W. Crabtree, Inorg. Chem. 23 3841 (1984).
38. S. Diaszank, M. Eschrodt, Phys. Stat. Sol., 72, 730 (1975).
39. E.A. Braude, J. Chem. Soc., 370 (1950) and earlier papers cited therein.
40. A. Laguren-Davidson, Ph.D. Dissertation, University of Cincinnati June, 1986.

Table I: Amounts of Anodic Charge and Formal Potentials at Various Scan Rates for Cu(II)-poly(2,5-thienylene)

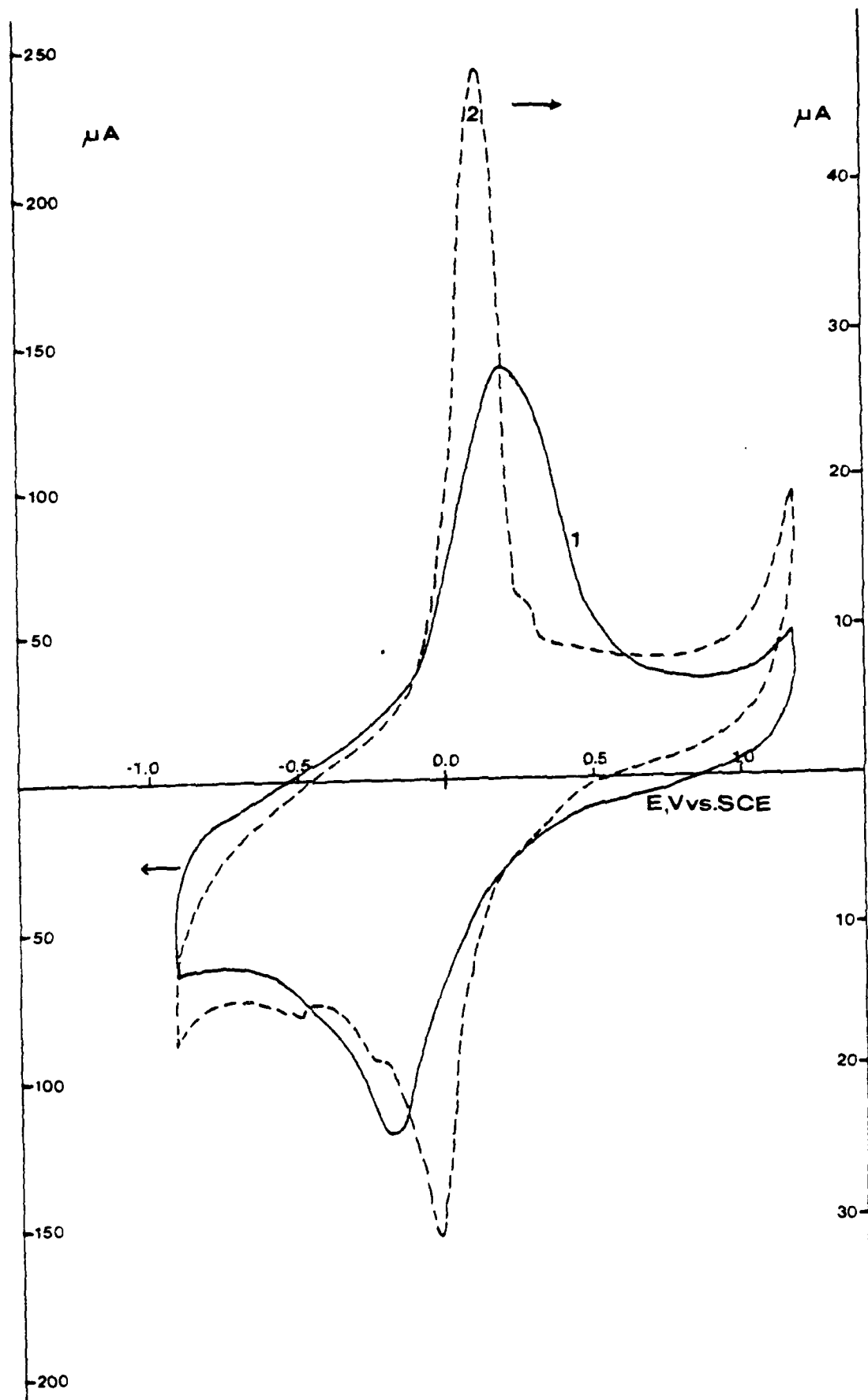
ν , mV s ⁻¹	Q , μ C cm ⁻¹	$E^{0'}$ mV
2	3000	7
5	2430	-3
10	1840	-3
20	1225	7
50	1125	-36
100	900	-28
200	770	-23
500	450	-27

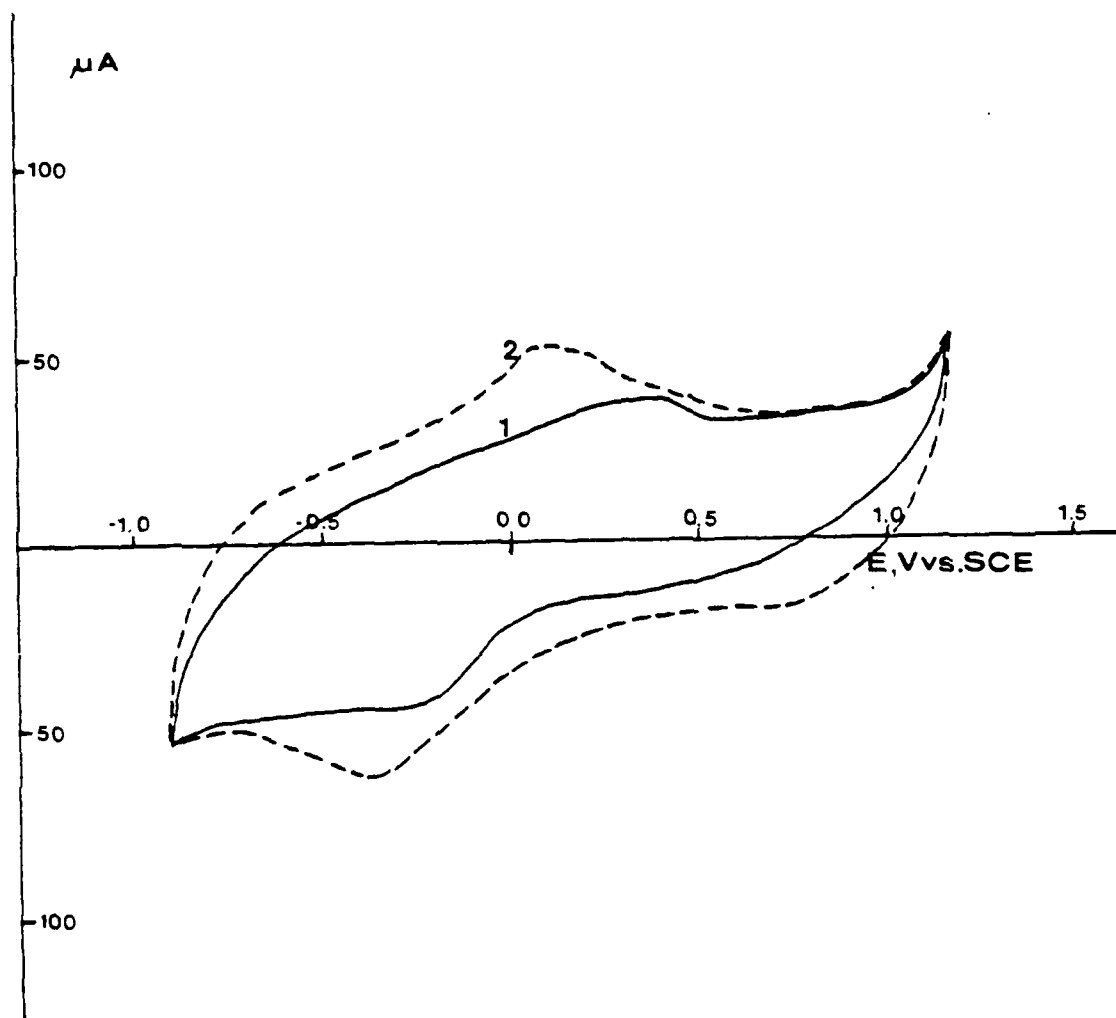
Table II: Formal Potential Values for Poly(thienylene) and Its Derivatives. Scan rate 100 mVs⁻¹.

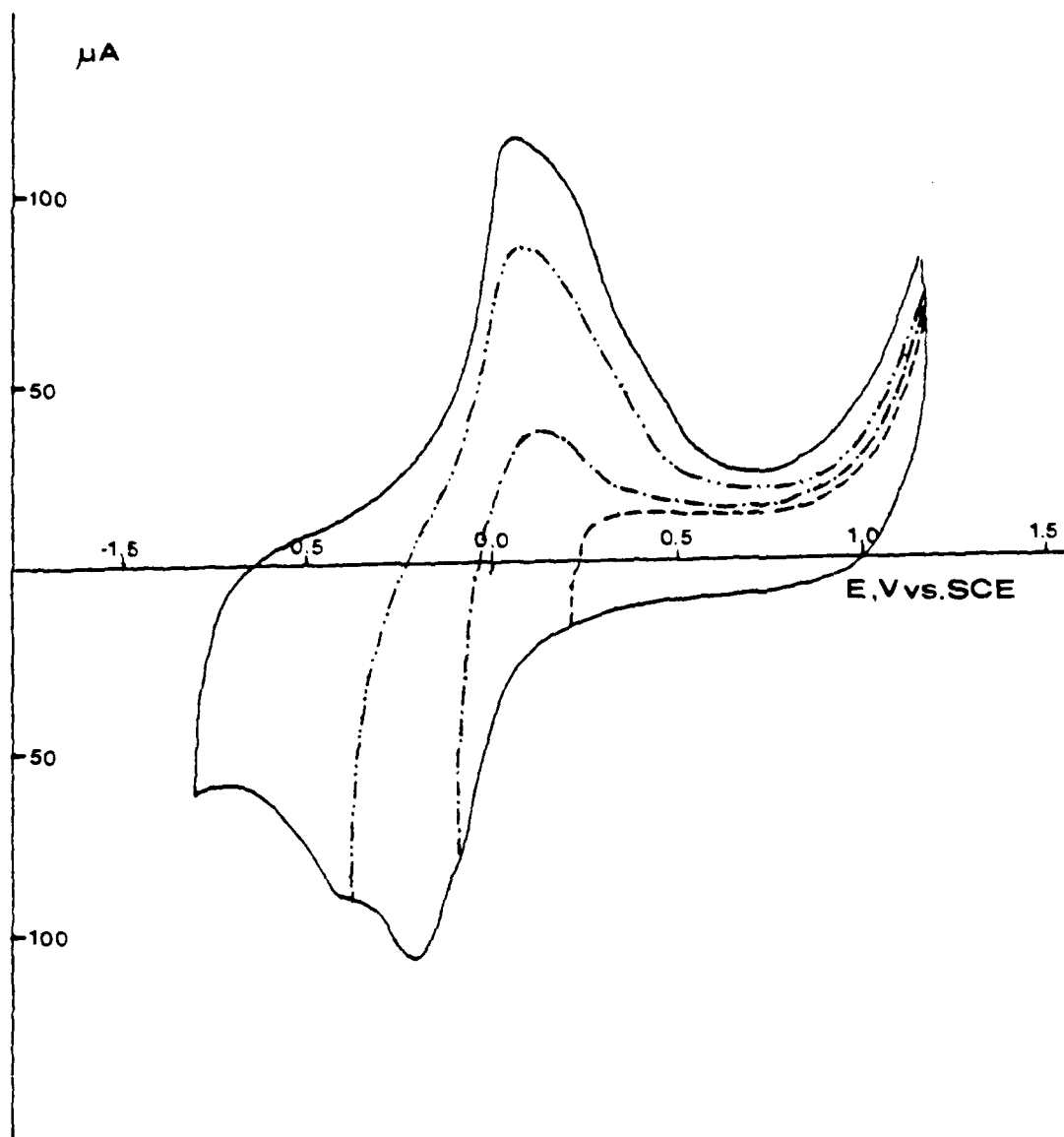
Polymer	Catalyst	E ^{0'} mV
	CuCl ₂	-28
	CuCl ₂	-56
	CuCl ₂	-24
	CuCl ₂	-33
	CuCl ₂	-23
	CuCl	-185

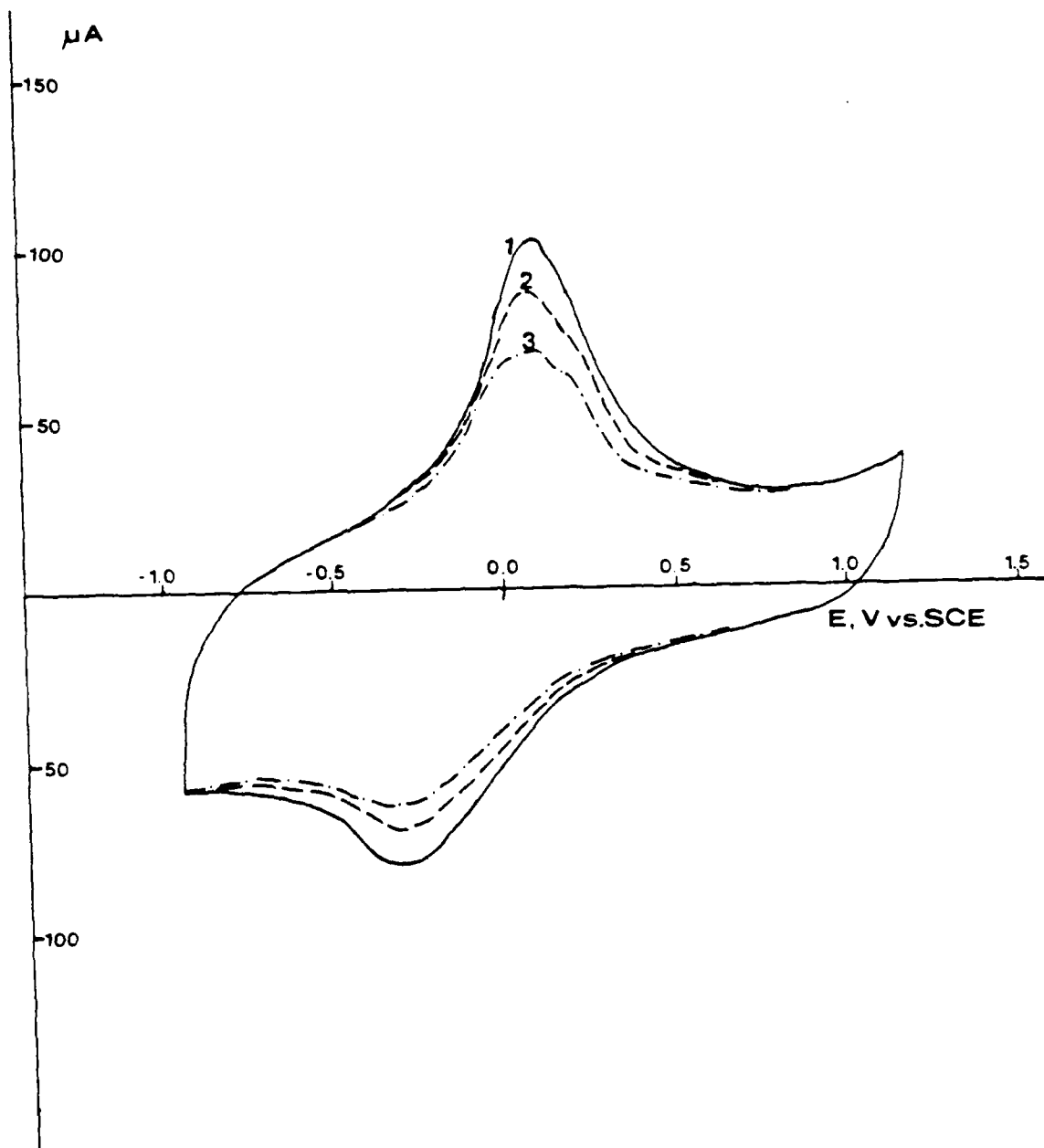
Figures

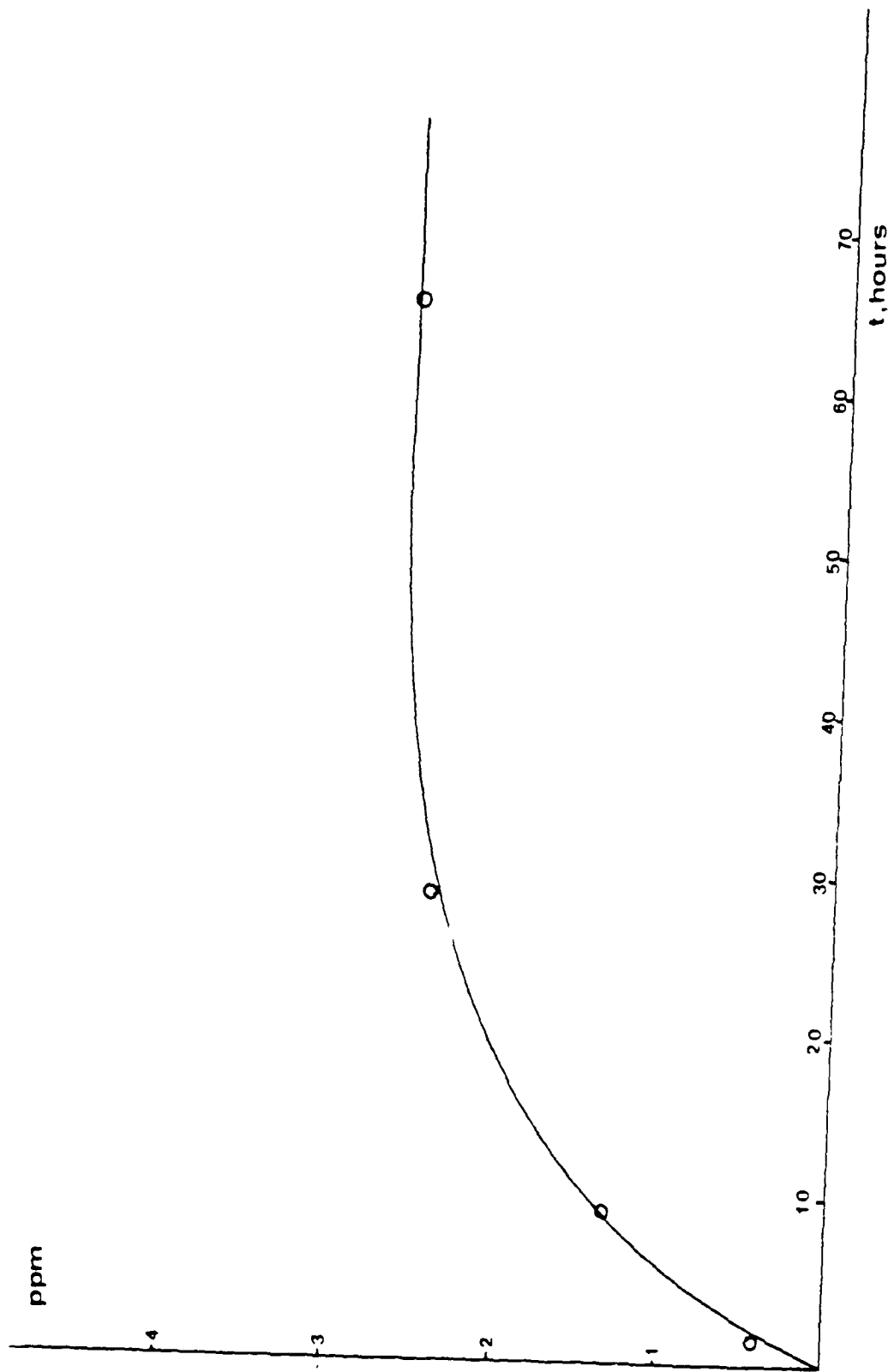
- Figure 1:** Cyclic voltammograms of Cu(II)-poly(2,5-thienylene) in 0.1 N NaClO₄ at different polarization rates: 10 mV·s⁻¹ (1) and 100 mV·s⁻¹ (2).
- Figure 2:** Cyclic voltammograms of Cu(I)-poly(2,5-thienylene) in 0.1 N NaClO₄: (1) after 2 sweeps (2) after 66 hr of cyclic polarization. Sweep rate 100 mV·s⁻¹.
- Figure 3:** Cyclic voltammograms of Cu(II)-poly(3-Sn(CH₃)₃-2,5-thienylene) in 0.1 N NaClO₄. Sweep rate 100 mV·s⁻¹.
- Figure 4:** Cyclic voltammograms of Cu(II)-poly(3-Si(CH₃)₃-2,5-thienylene) in 0.1 N NaClO₄: (1) unstirred, deaerated solution; (2) stirred, deaerated solution; (3) presence of O₂ in solution. Sweep rate 100 mV·s⁻¹.
- Figure 5:** Concentration of copper in solution (0.1 N NaClO₄) vs time of cyclic polarization from poly(2,5-thienylene). Sweep rate 100 mV·s⁻¹.
- Figure 6:** Cyclic voltammograms of polythienylenes in 0.1 N NaClO₄: Cu(II)-poly(3-Ge(CH₃)₃-2,5-thienylene), (1) first sweep, (2) third sweep, (3) after 14 hours of cycling. Cu(II)-poly(3-Sn(CH₃)₃-2,5-thienylene), (1) first sweep, (2) third sweep, (3) eighth sweep, (4) eleventh sweep. Sweep rate 100 mV·s⁻¹.
- Figure 7:** Cyclic voltammogram of Cu(II)-poly(2,5-thienylene) in 0.1 N NaClO₄ solutions: (1) H₂O, (2) D₂O. Sweep rate 100 mV·s⁻¹.
- Figure 8:** Cyclic voltammograms of polythienylenes in 0.1 N NaClO₄: (a) Cu(II)-poly(3-Si(CH₃)₃-2,5-thienylene) in 75% 1-butanol-25% water; (b) Cu(II)-poly(3-methyl-2,5-thienylene) in CH₃CN solution. Sweep rate 100 mV·s⁻¹.
- Figure 9:** Cyclic voltammograms of Cu(II)-poly(3-Si(CH₃)₃-2,5-thienylene) in (1) 0.1 N NaOH, (2) 0.1 N HClO₄. Sweep rate 100 mV·s⁻¹.
- Figure 10:** Cyclic voltammograms of Cu(II)-poly(3-Si(CH₃)₃-2,5-thienylene) in 0.1 N NaClO₄:
- (1) Solution contains 10⁻² N K₃Fe(CN)₃.
 - (2) After washing procedure -- in background solution (0.1 N NaClO₄).

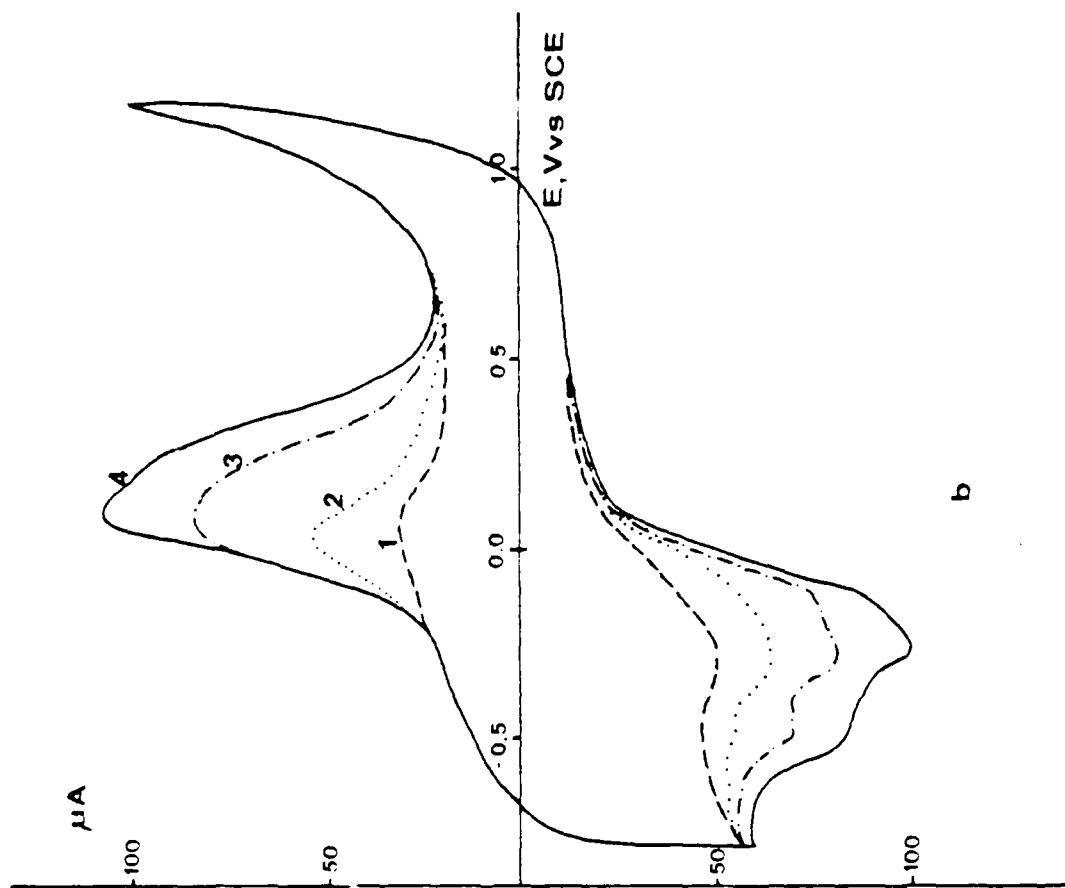
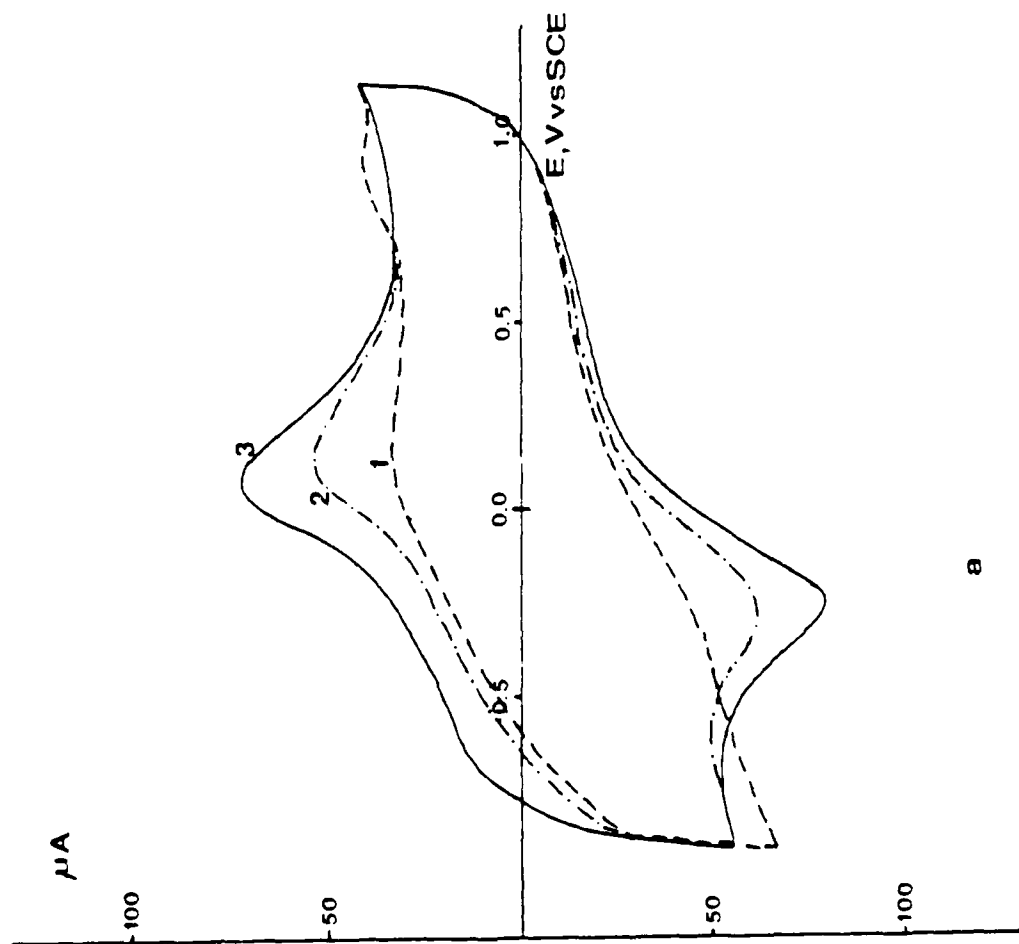


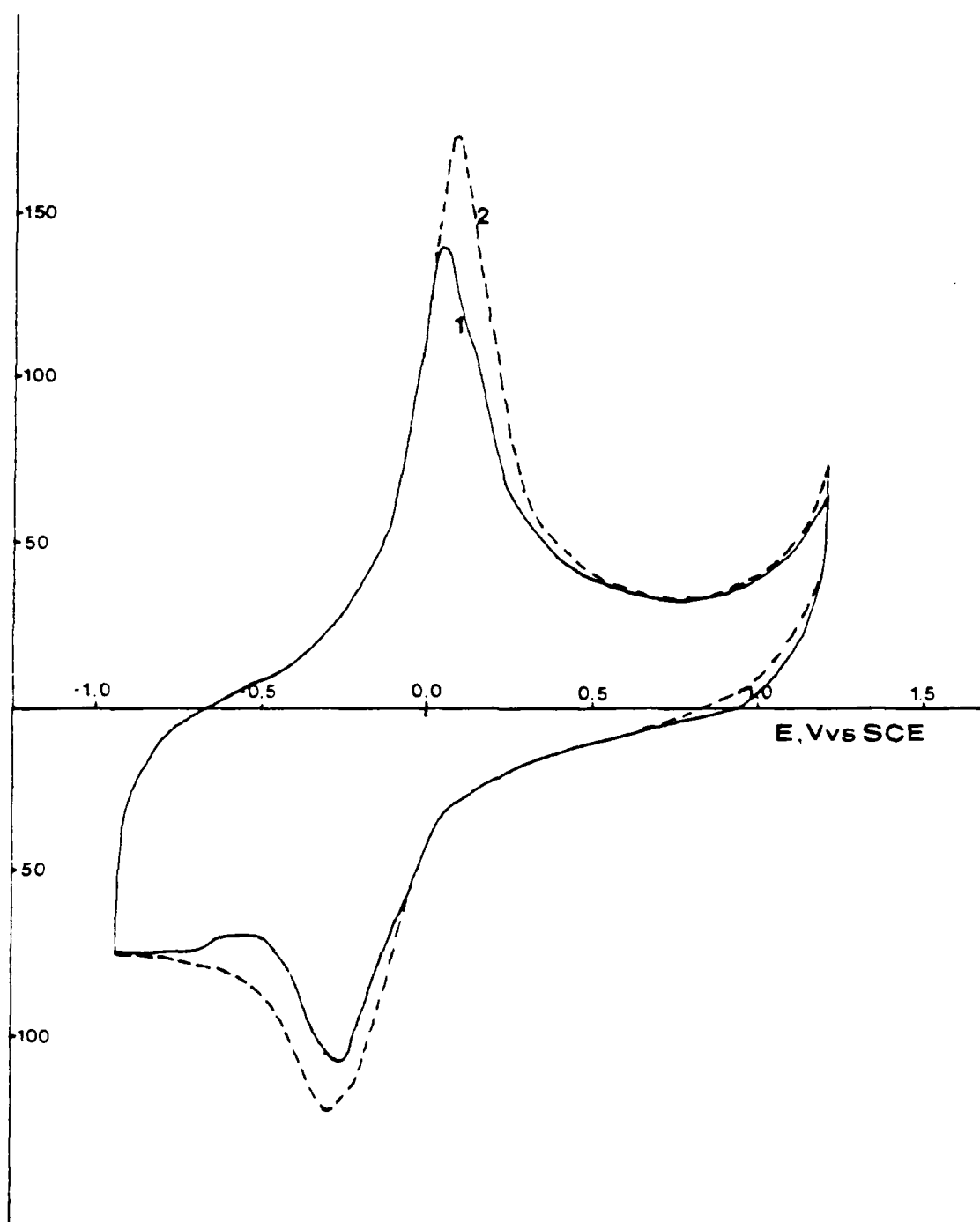


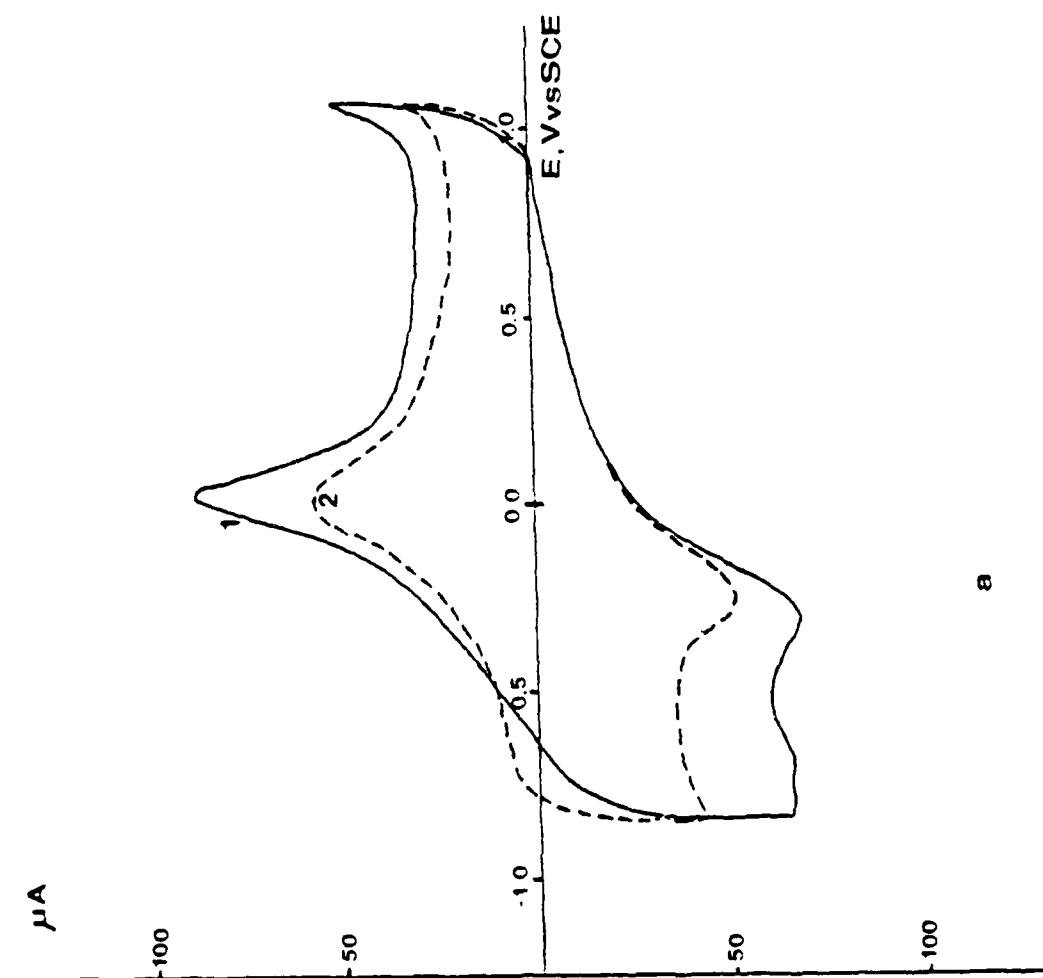
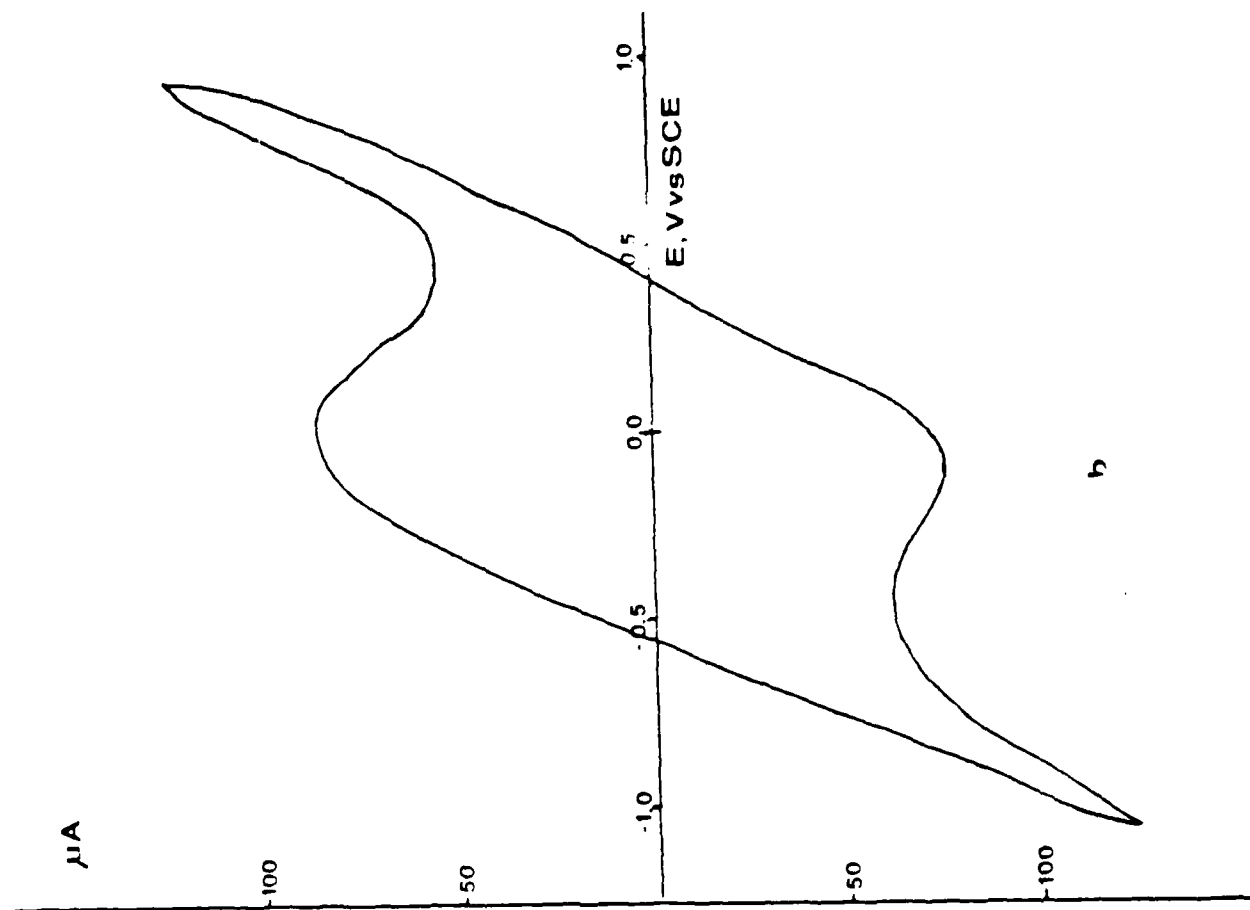


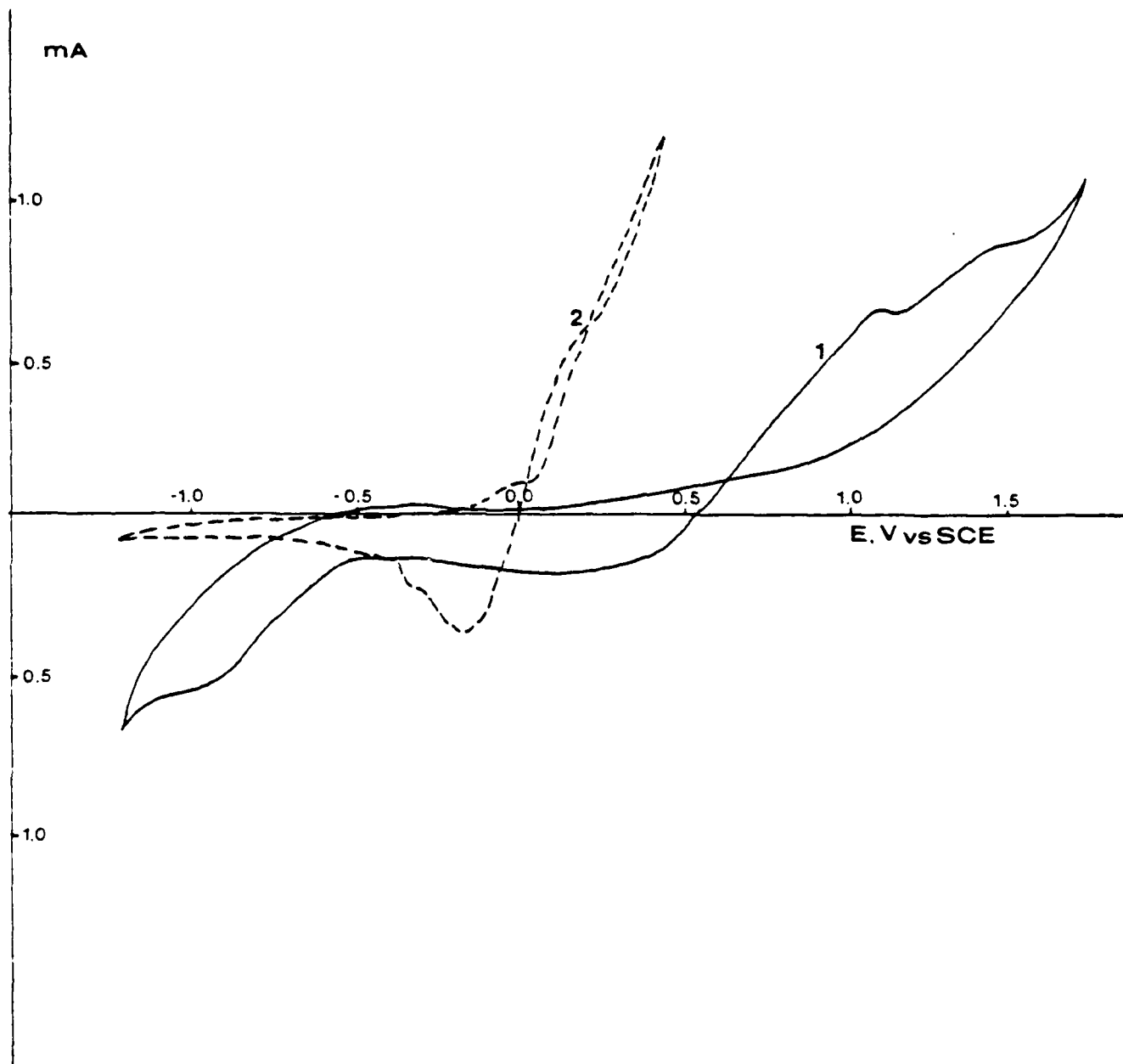


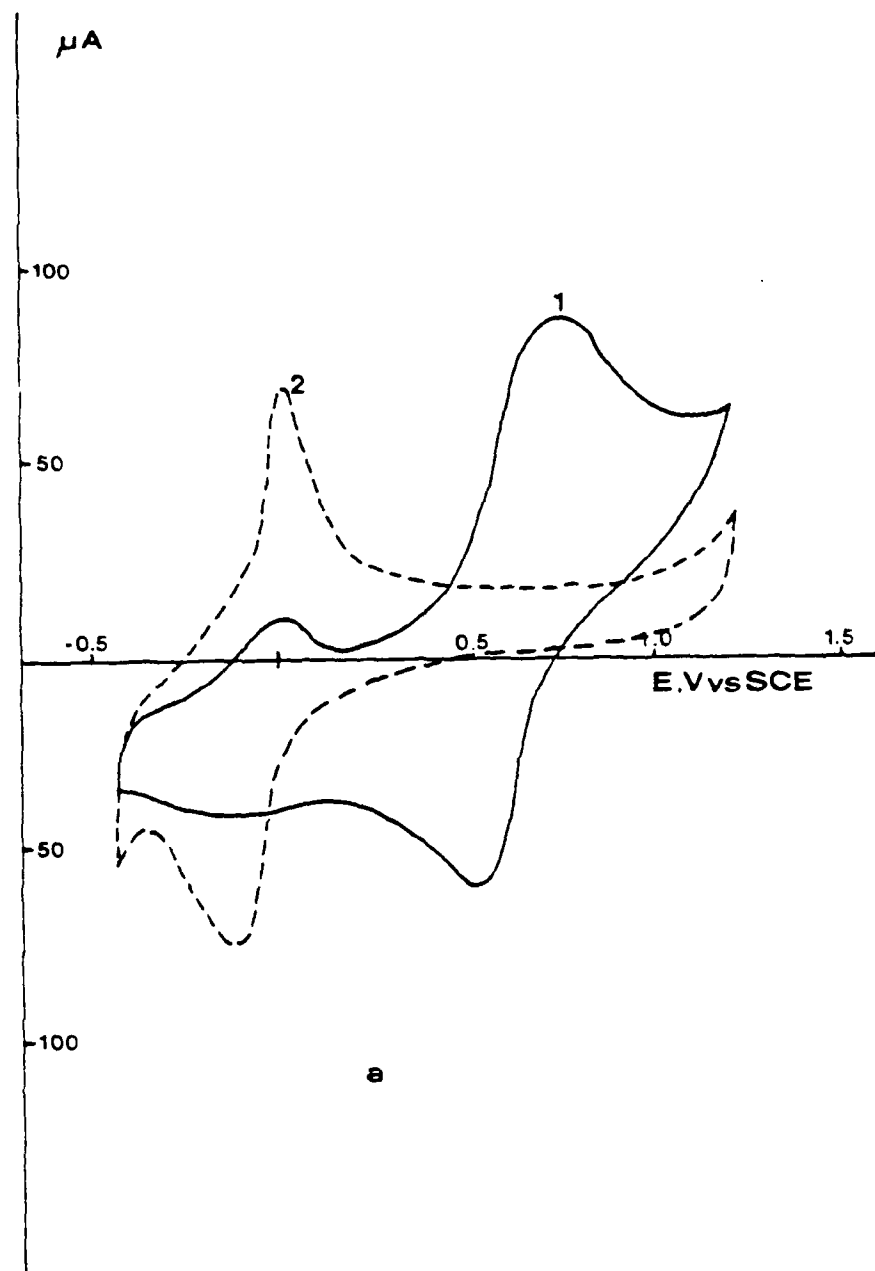












DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>	<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 92132
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southampton SO9 5NH
United Kingdom

Dr. J. Driscoll
Lockheed Palo Alto Research
Laboratory
3251 Hanover Street
Palo Alto, California 94304

Dr. D. N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, Utah 84602

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. Manfred Breiter
Institut für Technische Elektrochemie
Technischen Universität Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
Science Department
Lawrence Livermore National Laboratory
Livermore, California 94550

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. B. Brummer
EIC Incorporated
111 Downey Street
Norwood, Massachusetts 02062

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706

Library
Duracell, Inc.
Burlington, Massachusetts 01803

Electrochimica Corporation
20 Kelly Court
Menlo Park, California 94025-1418

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. M. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
Room 5E036 Forrestal Bldg., CE-14
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. John Wilkes
Air Force Office of Scientific
Research
Bolling AFB
Washington, D.C. 20332

Dr. R. Nowak
Naval Research Laboratory
Code 6171
Washington, D.C. 20375

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. B. P. Lever
Chemistry Department
York University
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
and Power Sources Division
Naval Weapons Support Center
Crane, Indiana 47522

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson
NAVSEA-56233 NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Dr. Carl Kannewurf
Department of Electrical Engineering
and Computer Science
Northwestern University
Evanston, Illinois 60201

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Robert Somoano
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus
NASA Headquarters
M.S. RTS-6
Washington, D.C. 20546

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. H. Tachikawa
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Dr. Theodore Beck
Electrochemical Technology Corp.
3935 Leary Way N.W.
Seattle, Washington 98107

Dr. Farrell Lytle
Boeing Engineering and
Construction Engineers
P.O. Box 3707
Seattle, Washington 98124

Dr. Robert Gotscholl
U.S. Department of Energy
MS G-226
Washington, D.C. 20545

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402

Dr. Martha Greenblatt
Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Dr. John Wasson
Syntheco, Inc.
Rte 6 - Industrial Pike Road
Gastonia, North Carolina 28052

Dr. Walter Roth
Department of Physics
State University of New York
Albany, New York 12222

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymer Science and Standards
Division
National Bureau of Standards
Washington, D.C. 20234

Ms. Wendy Parkhurst
Naval Surface Weapons Center R-33
R-33
Silver Spring, Maryland 20910

DL/413/83/01
359/413-2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. John Owen
Department of Chemistry and
Applied Chemistry
University of Salford
Salford M5 4WT ENGLAND

Dr. O. Stafsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

Dr. Boone Owens
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. S. G. Greenbaum
Department of Physics
Hunter College of CUNY
New York, New York 10021

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531
S-751 21 Uppsala, Sweden

Dr. Menahem Anderman
W.R. Grace & Co.
Columbia, Maryland 20144

END

DATED

FILM

8-88

Dtic